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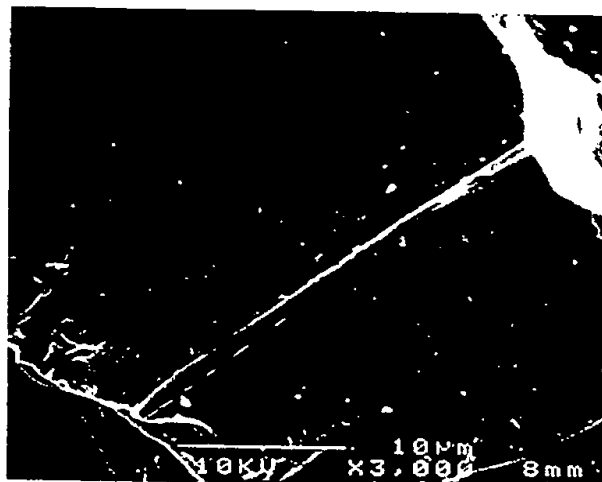
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(54) **MATERIAU DUR A REVETEMENT DE SURFACE, PROCEDE
DE FABRICATION ET UTILISATION DUDIT MATERIAU**

(54) **A SURFACE-COATED HARD MATERIAL, PRODUCTION
METHOD FOR THIS, AND USE OF THE SAME**



(57) Surface-coated hard material with a hardness ($HV_{0.2} \geq 10$ Gpa, the surface of which has a polysiloxane coating. Method for producing this, in which a hard grain is mixed with a polysiloxane, a polysiloxane emulsion, or a diluted polysiloxane emulsion. Use of a hard material of this type as a wear-reducing agent in lacquer coatings.

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Abstract

Surface-coated hard material with a hardness ($HV_{0.2}$) \geq 10 Gpa, the surface of which has a polysiloxane coating. Method for producing this, in which a hard grain is mixed with
5 a polysiloxane, a polysiloxane emulsion, or a diluted polysiloxane emulsion. Use of a hard material of this type as a wear-reducing agent in lacquer coatings.

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A Surface-Coated Hard Material, Production Method for This, and
Use of the Same

5 The present invention relates to a surface-coated
hard, mechanically resistant material, a method for its
production and its use.

10 It is known that coats of lacquer applied to flooring
laminates, genuine wood laminates, parquet, furniture, or to
wood or plastic panels in general can have resin added to them
in order to make them resistant to wear. When this is done,
lacquer systems based on phenol, melamine, aldehyde,
formaldehyde, urea, epoxy, polyester and/or polyurethane resins
are used. Preferred lacquer systems are the melamine resins.
Because of its hardness, transparency, inertness, and
availability, aluminum oxide or alumina products in the form of
15 fused corundum, sintered corundum, monocrystalline corundum
and/or calcined or sintered alumina such as plate-like alumina
are preferred for increasing the wear-resistance of the
coatings.

20 Published European Patent Application No. 0 732 449 A1
discloses a method for producing wear-resistant laminates, in
which the surface of the resin-impregnated paper that is used
during the production process is coated with a mixture
consisting of melamine resin, cellulose fibres, corundum as the
hard material, additives and water, and is dried to a specific
25 residual moisture content. The resin-impregnated paper is
processed within the laminate in the usual way. After the
laminate has been pressed and the melamine resin has hardened,
the corundum is firmly bonded into the resin layer, the wear
resistance of which is greatly increased because of the hardness

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of the corundum. Published German Patent Application No. 195 29 987 A1 discloses a method for producing highly wear-resistant lacquer coatings on a solid carrier, when wear-reducing material is either scattered directly onto the surface of the carrier and then covered with a synthetic-resin lacquer (acrylate resin, polyester resin, or polyurethane resin lacquer), or the wear-reducing agent is scattered onto the surface of the carrier that is already coated with lacquer. Generally speaking, when this is done, the wear-reducing effect of the resin increases as the grain size increases and as the degree to which the lacquer coating is filled increases. The maximum grain size that can be used, which is, at the same time, the optimal size, is determined by the thickness of the lacquer coating. However, the optimal degree of filling does not correspond to the possible maximum but is limited by the simultaneous demand for the highest possible degree of transparency of the lacquer coating. The subsequent pressing and hardening of the lacquer is effected by using known technology. One additional variant that is available in particular for laminates is that a transparent overlay paper that incorporates the appropriate resin is impregnated with lacquer then pressed onto the decorative layer and hardened. It is preferred that corundum be used as the wear-reducing agent.

Synthetic corundum is usually produced in an arc furnace, when the starting material--alumina or bauxite--is smelted at approximately 2000°C. In this process, the product is in the form of large blocks weighing several tonnes, and after cooling these are crushed and then processed into granular material. Typical areas of use for granular corundum, which is available in the most varied grades and grain sizes ranging from

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a few millimeters to several micrometers, are as grinding agents and refractory products. Because of its brittle-fracture behaviour, when the corundum is ground this results in a markedly fissured surface with many edge dislocations, micro-edges, grooving, and cracks. Similar grain surfaces with additional pores also seen in sintered or calcined alumina, particularly if they have been previously subjected to a grinding process. Grain surfaces of this kind display a high degree of capillarity with respect to low-viscosity liquids. Such grain characteristics have been found to be disadvantageous when processing aluminum oxide to form wear-resistant coatings.

According to the current state of the art, today, a wear-resistant lacquer coating is produced by a single application of the wear-reducing lacquer to which the hard granular material has already been mixed, subsequent drying, and pressing. When this is done, the particles of hard material lie, in part, directly on the surface of the protective coating so that, for example, dyes or other coloured liquids with a high level of creepage penetrate irreversibly into the micro-capillaries of these hard material particles thereby causing patches that cannot be removed from the laminate or lacquer surface. Attempts that have been made to avoid this effect by using low-viscosity lacquer systems that cover the whole of the granular material surface have been unsuccessful, since a minimum degree of viscosity is needed in order to achieve the desired thickness of the lacquer coating.

A further disadvantage of the markedly fissured surfaces of the hard granular material that cannot be completely wetted with lacquer is the fact that light is scattered diffusely on the above-discussed micro-edges, cracks, and edged

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degree of transparency is one of the most important criteria for these coatings, which are frequently used in applications in which the visual effect plays a major role. In addition to this, small air bubbles can accumulate on these micro-edges and cracks, and this causes an additional diffuse scattering of the light, with the result that transparency is still further degraded.

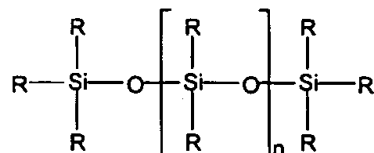
Thus, it is the objective of the present invention to provide granular hard material that does not suffer from the disadvantages described heretofore.

This objective has been achieved with a hard material whose surface bears a polysiloxane coating. The polysiloxane-coated material can be produced by mixing the grains of the hard material with a polysiloxane solution, emulsion or diluted emulsion.

This is realized concretely by a hard material with a Vickers hardness measured under a load of 0.2 kg, $HV_{0.2} \geq 10$ GPa, preferably ≥ 15 GPa, the surface of which is covered with a polysiloxane coating. The measurement of Vickers hardness, which is defined in German Industry Standard DIN 50 133, is a well-known method to characterize the hardness of materials. The value of the Vickers hardness is proportional to the quotient of the testing force (for testing done under a load of 0.2 kg, force = $0.2 \text{ kg} \cdot 9.81 \text{ m sec}^{-2} = 1.96 \text{ N}$) and the superficial area (mm^2) of the indentation in the hard material.

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It is preferred that the treatment of the hard material be effected with a solution, emulsion, or diluted solution of a polysiloxane of the following formula:



- 5 wherein the R radical can in each instance be a hydrogen, alkyl and/or phenyl group, and n stands for an integer from 1 to 100. Especially good results are achieved if the organic R radical is a methyl group.

10 Surface treatments or coatings with particles of hard materials have been known for a considerable time and are used for the most varied purposes. For instance, European Patent No. 0 387 748 describes a hydrophobically coated grinding grain that is based on corundum and/or silicon carbide, the surface of which is treated with highly dispersed hydrophobic silicon oxide
15 so that the strength with which the grain is bonded into the synthetic resin is improved. Similarly, according to European Patent No. 304 616, an improvement of the bonding of grinding grains in a plastic resin system is achieved by surface treatment with hygroscopic and/or hydrophobic substances. In
20 addition, this treatment entails the additional effect that granular material treated in this way disperses better in the electrostatic field.

It is also usual to coat the grains with a binder and a pigment in order to increase the surface area of the grain,
25 thereby once again enhancing the way in which the grain is bound in when grinding agents are manufactured. This coating also has

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the effect of simultaneously improving the dispersability of the granular material. However, none of the above treatments can compensate for the disadvantages of aluminum oxide when it is used in lacquer coatings or laminates (a high degree of capillarity as compared to low-viscosity liquids and diffuse dispersion of the light).

On the other hand, if one mixes hard granular material based on aluminum oxide with polysiloxanes or corresponding emulsions or solutions, because of the outstanding creep behaviour of the polysiloxanes one achieves complete coating of the surface of the individual grains, when the micro-edges, cracks, grooves, and offset edges are covered over or filled so that low-viscosity liquids can no longer penetrate into the grain and there is no longer any diffuse dispersion of light on the cracks or edges.

Hard material based on aluminum oxide can be electro-smelted corundum, monocrystalline corundum, sintered corundum, tabular alumina, calcined or sintered alumina products, such as plate-form alumina, or mixtures of these. There are no restrictions as to the size of the grain for the hard material that is to be used. Depending on the requirement and the application, both micro- as well as macro-granular material can be treated according to the present invention. However, the hardness of the hard grains should have a minimum value of 10 GPa, preferably 15 GPa, in order to provide adequate protection against wear. The processing itself is effected in the known manner by spraying on an appropriate solution, emulsion or diluted emulsion of a polysiloxane or by mixing the hard material with a solution, emulsion or dilute emulsion of a polysiloxane in suitable mixers (tumbling mixers, rotary mixers,

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staggered-baffle drum mixers, and/or intensive mixers). The emulsion or dilute emulsion of a polysiloxane that is used is preferably an aqueous emulsion. Depending on the moisture content of the starting granular material, it has been found

5 advantageous to subject the material to heat treatment in a temperature range between 100°C and 600°C immediately prior to the coating process, in order to eliminate any moisture that is adhering to the surface, including the pores and cracks. The quantity and concentration of the polysiloxane solution must be

10 so selected that the complete surface of each individual grain is covered once it has been treated. The finer the grain size of the material that is to be treated the greater will be the quantity of polysiloxane that will have to be used. For reasons of economy, it is best at to apply a complete coating that is as

15 thin as possible. The quantities of polysiloxane that will be required for a complete coating lie between 0.001 and 10 wt.%, preferably between 0.01 and 5 wt.%, most preferably between 0.1 and 5 wt.%, relative to the hard material that is used. For the reasons given heretofore, it is preferred that the quantity of

20 polysiloxane that is used during the treatment range between 0.1 and 1.5 per cent by weight relative to the hard material that is used, preferably between 0.5 and 1.5 per cent. The quantity used will depend on the grain size or the specific surface area of the grinding grain. The advantageous effect varies very

25 little even if the optimal quantities are exceeded over a relatively large range. The viscosity of the polysiloxane or of the corresponding emulsion, diluted emulsion, or solution that is used should not exceed 1500 mPa*s, preferably 1000 mPa*s, at room temperature in order to achieve the optimal effect of the

30 coating. Once coated with the polysiloxane solution, emulsion,

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or diluted emulsion, the hard material is dried in a temperature range between 100°C and 400°C, preferably between 100°C and 200°C.

In addition to improved visual properties of the lacquer and laminate coatings, most surprisingly, when the hard material treated according to the present invention was incorporated it was found that the resistance to wear of these layers is higher than comparable layers in which untreated hard material is incorporated. A preferred embodiment of this invention is, therefore, the use of this hard material as a wear-reducing agent in lacquer coatings based on phenol, melamine, aldehyde, urea, formaldehyde, epoxy, polyester, and/or polyurethane resins, or in transparent overlay papers to manufacture wear-resistant lacquer coatings. Resistance to wear was determined using the Taber method, whereby a test body is rotated beneath loaded, cylindrical adhesive wheels that are covered with defined abrasive paper and the number of rotations required in order to achieve a specific degree of wear is then measured.

One possible explanation for this surprising effect maybe the good gliding quality and lubricating quality of the polysiloxane. The wear test itself is nothing more than a grinding process and the use of lubricant such as oil when grinding is a generally known technique that is used in order to reduce the coefficient of friction between the material and the grinding agent and thus reduce the aggressiveness of the grinding agent. In the present case it is possible that the effect of the grinding paper is reduced and wear on the lacquer or laminate layer is also reduced.

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The present invention will be described in greater detail below on the basis of embodiments shown in the following examples and the accompanying drawings, without necessarily being restricted to these.

5 Figure 1 is an electron micrograph of a surface of untreated hard grain (Enlargement 3000x).

Figure 2 is an electron micrograph of the surface of grain treated according to the present invention (Enlargement: 3000x).

10 Figure 3 is a surface of a lacquer coating with untreated hard grains.

Figure 4 is a surface of a lacquer coating with hard grains coated according to the present invention.

Examples 1 - 5

15 1 kg pure white corundum (Alodur[®] WSK, Treibacher Schleifmittel), F 280 granulation, was tempered at 400°C and then sprayed with a diluted, aqueous polysiloxane emulsion
(Baysilone[®] oil emulsion H, Bayer Leverkusen) when in a drum mixer, after which it was mixed intensively for 20 minutes. The
20 coated granular material was then dried for 20 minutes at 120°C in a convection oven. Subsequently, the total content of SiO₂ and the proportion of polysiloxane on the surface of the grains was determined.

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Ex.	Baysilone Oil Emulsion H	Total content SiO ₂ (wt.%)	Content (wt.%) Polydimethylsiloxane
1	1 ml in 15 ml H ₂ O	0.032	0.025
2	5 ml in 15 ml H ₂ O	0.135	0.128
3	15 ml (undiluted)	0.589	0.582
4	30 ml (undiluted)	1.309	1.302
5	60 ml (undiluted)	2.743	2.704
6*	-	0.007	-

* untreated comparison material

Table 1: Concentration series

5 The best results in this series were obtained with
Example 4. Descriptions were based on electron microscope
imagery and measurements of wear values as compared to untreated
granular material.

10 In the Appendix, Figure 1 shows the untreated granular
material (Example 6) with a very finely structured and fissured
surface. In comparison to this, Figure 2 shows the grain
surface (Example 4), which is completely covered by the coating
according to the present invention. The cracks are closed and
have been filled to a large extent. The edges are rounded, and
no more edge displacements can be seen. Figures 3 and 4 in the
15 Appendix serve to document the effect of the coating according

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to the present invention on the transparency of a lacquer coating. Whereas the uncoated grains (Example 6) can be clearly seen in the lacquer coating, and a relatively large number of intracrystalline optical refractive edges can be seen, the hard grains coated according to the present invention, shown in Figure 4, can only be identified poorly by the grain-resin boundary. There are absolutely no intra-crystalline visual refractive edges to be seen.

Table 2 sets out the IP wear values as determined by Draft Standard prEN 13329:1998, Appendix E

Example	IP Average value from three test bodies	wear resistance compared to untreated grain
1	2200	105%
2	2200	105%
3	2300	109%
4	2500	119%
5	2500	119%
6*	2100	100%

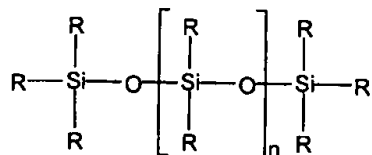
Table 2: Wear values

The test bodies that contained the coated hard grain (Example 4) according to the present invention display enhanced wear resistance that is 19% greater as compared to Example 6.

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CLAIMS:

1. Surface coated hard material with a hardness (HV_{0.2}) ≥ 10 GPa, the surface of which has a polysiloxane coating.
2. Surface coated hard material as defined in Claim 1,
5 characterized in that the hardness (HV_{0.2}) ≥ 15 Gpa.
3. Surface coated hard material as defined in Claim 1 or Claim 2, characterized in that aluminum oxide is the basis of the hard material.
4. Surface coated hard material as defined in Claim 3,
10 characterized in that the basis of the hard material consists of electro-smelted corundum, monocrystalline corundum, sintered corundum, sintered alumina and/or calcined alumina, or mixtures of these.
5. Surface coated hard material as defined in any one of
15 Claims 1 to 4, characterized in that the surface of the hard material is coated with a polysiloxane of the formula:



6. Surface coated hard material as defined in Claim 5,
characterized in that the R radical is hydrogen, an alkyl and/or
20 phenyl group.
7. Surface coated hard material as defined in Claim 5 or 6, characterized in that n is an integer between 1 and 100.

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8. Surface coated hard material as defined in any one of Claims 5 to 7, characterized in that the R radical is a methyl group.

9. Surface coated hard material as defined in one of the
5 Claims 1 to 8, characterized in that the quantity of polysiloxane on its surface amounts to 0.001 to 10 wt.% relative to the hard material that is used.

10. Surface coated hard material as defined in Claim 9,
characterized in that the quantity of polysiloxane amounts to
10 0.01 to 5 wt.%.

11. Surface coated hard material as defined in Claim 9 or 10, characterized in that the quantity of polysiloxane amounts to 0.1 to 5 wt.%.

12. Surface coated hard material as defined in any one of
15 Claims 9 to 11, characterized in that the quantity of polysiloxane amounts to 0.1 to 1.5 wt.%.

13. Surface coated hard material as defined in any one of Claims 9 to 12, characterized in that the quantity of polysiloxane amounts to 0.5 to 1.5 wt.%.

20 14. Method for producing a hard material as defined in any one of Claims 1 to 13, characterized in that a hard material grain is mixed with a polysiloxane or a polysiloxane emulsion.

15. Method as defined in Claim 14, characterized in that the hard material is mixed with a diluted polysiloxane emulsion.

25 16. Method as defined in Claim 14 or 15, characterized in that the hard grain is subjected to a heat treatment in a

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temperature range between 100°C and 600°C prior to the mixing process.

17. Method as defined in any one of Claims 14 to 16, characterized in that once coated with polysiloxane the hard
5 grain is dried in a temperature range between 100°C and 400°C.
18. Method as defined in Claim 17, characterized in that the drying temperature is between 100°C and 200°C.
19. Method as defined in any one of Claims 14 to 18, characterized in that an aqueous polysiloxane emulsion is used.
- 10 20. Method as defined in any one of Claims 14 or 16 to 19, characterized in that the viscosity of the polysiloxane or the polysiloxane emulsion that is used is below 1500 mPa*s.
21. Method as defined in any one of Claims 15 to 19, characterized in that the viscosity of the diluted polysiloxane
15 emulsion that is used is below 1500 mPa*s.
22. Method as defined in Claim 20, characterized in that the viscosity of the polysiloxane or the polysiloxane emulsion that is used is below 1000 mPa*s.
23. Method as defined in Claim 21, characterized in that
20 the viscosity of the diluted polysiloxane emulsion that is used is below 1000 mPa*s.
24. Use of a hard material as defined in any one of Claims 1 to 13 as a wear-reducing agent in lacquer coatings based on phenol, melamine, aldehyde, urea, formaldehyde, epoxy,
25 polyester, and/or polyurethane resins.

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25. Use of a hard material as defined in any one of Claims 1 to 13 as a wear-reducing agent in transparent overlay papers to manufacture wear-resistant lacquer coatings.

FETHERSTONAUGH & CO.

OTTAWA, CANADA

PATENT AGENTS

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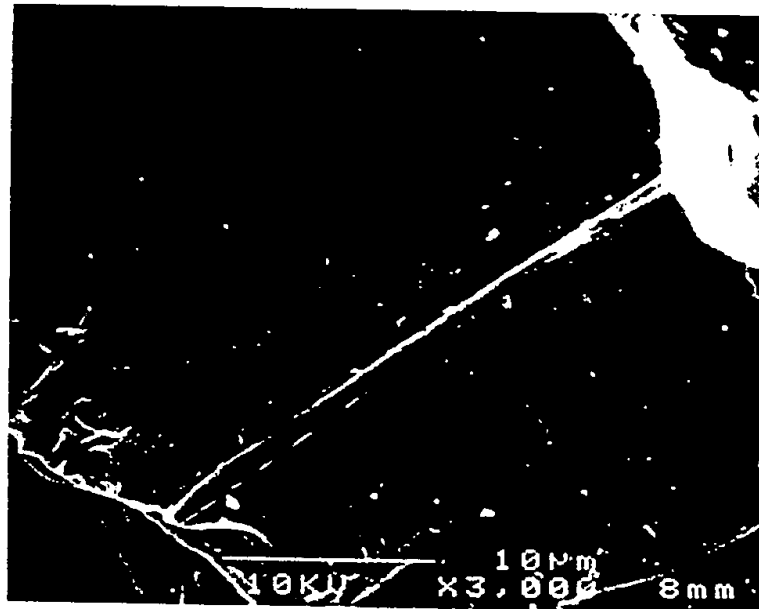


FIG. 1

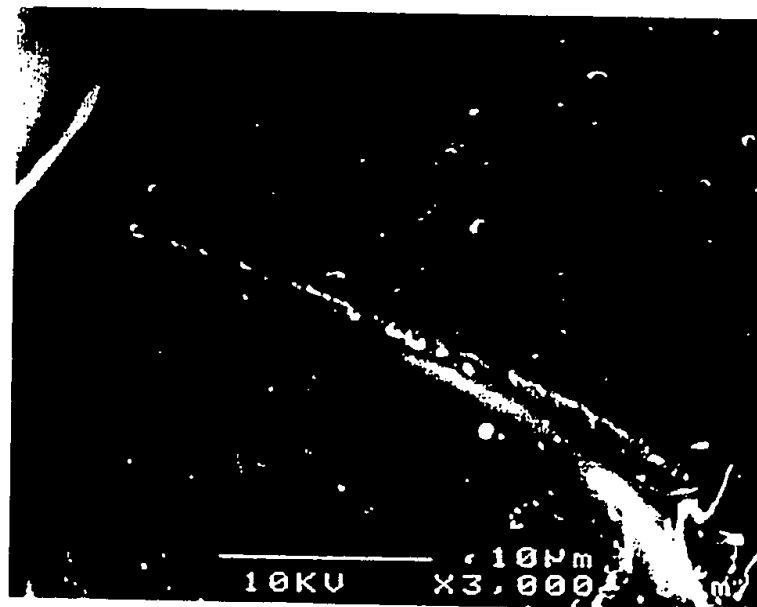


FIG. 2

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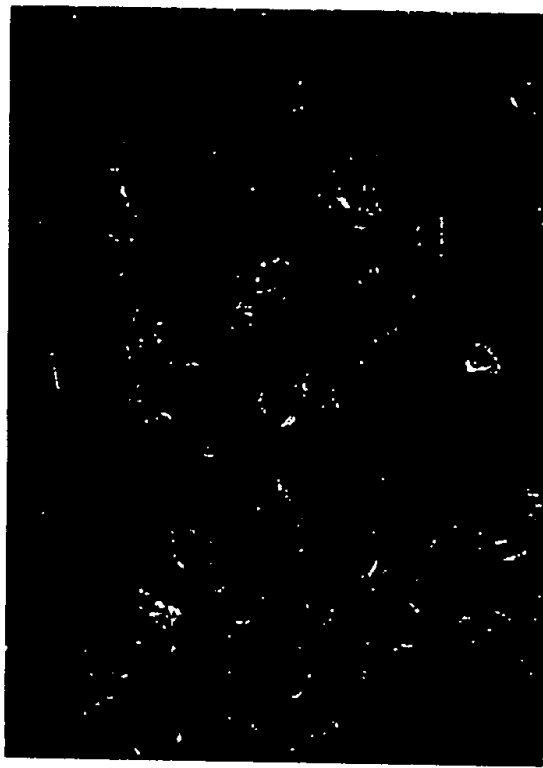


FIG. 3



FIG. 4

